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Note

THERMAL BEHAVIOUR OF MORPHOLINIUM PERCHLORATE

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Morpholine is a base of moderate strength, comparable with that of ammonia, and capable of forming -onium-type salts. Extensive studies [1,2] have been made on the thermal stability of ammonium perchlorate because of its technological use as an oxidant in solid state rocket propellants. The preparation, characterization and thermal behaviour of morpholinium perchlorate are reported in this note. The study was followed by XRD, IR, TG, DTA and mass spectral techniques.

EXPERIMENTAL

Morpholinium perchlorate (MP) was prepared by neutralizing 20 ml 40% morpholine by the addition of 20 ml 20% perchloric acid. The resultant solution was concentrated over a water-bath and the separated crystals were filtered, washed with an acetone—ether mixture and recrystallized from methanolic solution. Analytical results were: found C 25.82, H 5.68, N 7.32%; calcd. for $C_4H_{10}NO_5Cl$, C 25.64, H 5.37, N 7.46%; m.p. 173°C.

The X-ray powder diffraction patterns were taken on a Philips diffractometer using Cu$K\alpha$ radiation, and the IR spectra were recorded on a Perkin—Elmer 257 spectrometer using the KBr pellet technique.

TG and DTA studies were made in air using a Stanton thermobalance and a Netzsch differential thermal analyzer, whereas in an atmosphere of argon, a Mettler thermal analyzer was employed. Mass spectral analyses were made using a Varian mass spectrometer in a quartz crucible, with the filament operating at 70 eV and 300 μA.

RESULTS AND DISCUSSION

The crystals of MP are colourless, non-hygroscopic and stable in air. The powder patterns of the compound gave the following d_{hkl} values (in Å) when the incident angle 2θ was scanned from 5 to 70°: 6.83w, 6.28w, 4.92s, 4.80w, 4.22s, 3.81s, 3.55w, 3.17m, 3.06m, 3.03s, 2.91w, 2.65w, 2.34w,

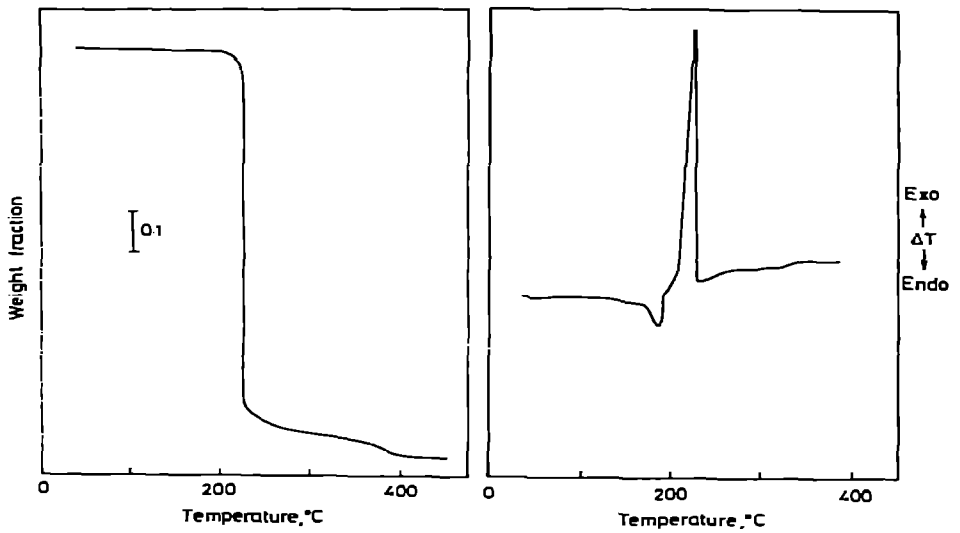

Fig. 1. TG and DTA plots of morpholinium perchlorate.

TABLE 1

Mass spectral results of morpholinium perchlorate

m/e	Ion (m^+)	Intensity (%)
15	NH	8
17	OH	6
18	H_2O	32
27	NCH	24
28	CO	97
29	$HNCH_2$	100
30	CH_2O, NO	65
35	Cl	6
36	HCl	33
41	H_3CCN	13
42	C_2H_4N	43
43	C_2H_4NH	13
44	CO_2, N_2O	65
51	ClO	15
55	C_3H_5N	9
56	C_3H_6N	69
57	C_3H_6NH	98
58	$C_3H_6NH_2$	14
67	ClO_2	46
83	ClO_3	48
86	C_4H_8ON	54
87	C_4H_8ONH	100
88	$C_4H_8ONH_2$	5
100	$HClO_4$	30
114	?	37
115	?	35

2.23w, 1.69w and 1.36w. The IR spectrum of the compound exhibited characteristic bands due to the NH_2 group [3] at 3000 (ν_{NH_2}) and 1580 cm^{-1} (δ_{NH_2}). The strong band at 1100 cm^{-1} and a weak absorption at 980 cm^{-1} corresponded to the ClO_4 group [4].

The TG and DTA curves of MP in air are given in Fig. 1, and are identical to those obtained in an atmosphere of argon. The TG curve suggests that the compound starts decomposing at 200°C and about 95% of initial weight is lost at 245°C. No residue remains at 400°C when heated in air, whereas the unoxidized carbonaceous matter was present in the atmosphere of argon. No chlorate or chlorite is found during the decomposition, as evidenced by the absence of the characteristic Cl—O stretching frequencies in the IR spectrum of the partially decomposed MP. The DTA curve exhibits an endotherm at 174°C which is ascribed to the melting, and an exotherm at 230°C due to the oxidative decomposition of the compound.

The mass spectral peaks obtained at 150°C, along with the probable assignments, are given in Table 1. The results suggest no indication of an MP ($C_4H_{10}NO_5Cl$) molecular peak, which leads us to believe that the decomposition takes place by proton transfer, as in the case of ammonium perchlorate [5]. It is found that the spectral fragments at 90 and 120°C are almost identical to the major fragments $HClO_4$ and HCl, in addition to those of the morpholine moiety [6,7] and its oxidized products. However, at 150°C, in addition to these fragments, Cl, ClO, ClO_2 and ClO_3 are also predominant. It is interesting to note that in the case of NH_4ClO_4, at low temperatures, although O_2 is one of the products [2], in the present case only a negligible amount of O_2 is present, probably due to its oxidative reaction with the organic moiety.

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